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Preparation of 2, 4-Dichloro-α-Chlorostyrene

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PREPARATION OF 2,4-DICHLORO-α-CHLOROSTYRENE

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

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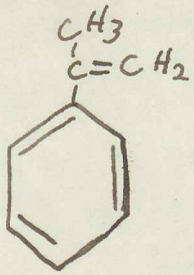
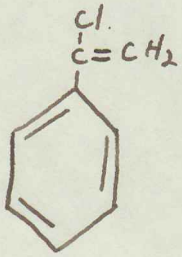
INTRODUCTION

Styrene and various substituted styrenes have found wide application in the formation of polymers and copolymers, such as synthetic rubbers. Substituted styrenes have been investigated in attempts to develop polymers with special physical properties, a high dielectric constant for an example. α -Methylstyrenes have been successfully copolymerized by Bachman and Finholt (1) while α-chlorostyrene seems unreactive toward polymerizing agents.

Figure I



α-Methylstyrene



α-Chlorostyrene

It was the purpose of the present investigation to develop a preparation of a nuclear substituted α-chlorostyrene, namely 2,4-dichloro-α-chlorostyrene, that might exhibit an increased reactivity toward polymerization because of an unbalancing effect (see discussion).

A further purpose was to prepare α-chlorostyrene by the method of Dufraisse and Viel (3) and check its physical constants against their values.

HISTORICAL ASPECTS

The synthesis worked out by Dufraisse and Viel (3) affords an efficient and simple preparation of α-chlorostyrene. This method was followed by Coleman (2) in his work on α-chlorostyrenes and was also used in the current investigation. This method involved the equimolecular reaction between acetophenone and PCl_5. A molar quantity of HCl was liberated by this reaction and tended to add across the newly formed double bond. This addition was readily prevented by carrying out the reaction in a solvent in which hydrogen chloride was insoluble. It was also found that an elevated temperature was necessary for a complete reaction. On standing, α-chlorostyrene decomposed to chlorobenzene and formaldehyde, which was followed by resinification (3).

More recently, Emerson and Agnew (4) reported the preparation of α- and β-chlorostyrene. This method involved the dehydrohalogenation of 1-phenyl-1,2-dichloroethane by the use of alcoholic sodium hydroxide solution.

The preparation of 2,4-dichloro-α-chlorostyrene also required a synthesis of the starting material, 2,4-dichloroacetophenone. Marshall (12) reported the preparation of acetophenone from methylmagnesium iodide and an excess of benzaldehyde. Gilman and Nelson (7) and Gilman and Mayhue (6) have prepared substituted acetophenones from methyl Grignard reagents and substituted benzoyl chlorides. Roberts and Turner (15) have outlined a Friedel and Crafts type synthesis for di-halogen substituted acetophenones. In the present investigation it was found that the method of Roberts and Turner was the only one acaptable to the preparation of 2,4-dichloroacetophenone.

EXPERIMENTAL WORK

Preparation of α-Chlorostyrene

The method of Dufraisse and Viel (3) was employed. A one liter three neck flask was fitted with a thermometer and a reflux condenser. An HCl gas trap as suggested by Gilman and Blatt (5) was attached to the top of the condenser. The flask was charged with 94.9 g. (.79 moles) of acetophenone, 165 g. (.79 moles) of PCl_5, and 400 ml. petroleum ether and the mixture was refluxed for two and one-half hours. A temperature rise from 37° to 60° was noted during the course of the reaction.

The reaction mixture was then filtered to remove any unreacted PCl_5, and the solvent was removed by distillation. The crude product was then roughly distilled using a water vacuum pump; liquid boiling under 108° at 25 mm. was collected. In order to obtain a pure sample, the distillate was fractionated in a 70 cm. adiabatic, packed rectification column. A 7.8 g. fraction boiling at 68° at 9 mm. was collected. The extremely low yield was due to lack of experience in operating the rectification column.

The α-chlorostyrene distilled over as a clear colorless liquid, but after a few hours exposure to the air it turned dark green. It was necessary to distill a fresh sample before use.

The density of the purified compound, determined with a pyknometer, was $D\ 27^{\circ}/27^{\circ} = 1.065$ g/ml. Dufraisse and Viel (3) found it to be 1.1028 g/ml. at 20.5°. The refractive index with reference to the Sodium "D" line at 25° was found to be 1.5585. Coleman (2) gave $n_D^{20^{\circ}} = 1.5585$, and Dufraisse

and Viel gave $n_D^{20.5^\circ}$=1.5504.

The chlorine content of the compound was determined by the method outlined by Stepanow (17). A mixture of 1.190 g. α-chlorostyrene, 190 ml. ethyl alcohol, and 12 g. sodium were refluxed. When the sodium dissolved, 40 ml. water was added and the alcohol was distilled off the remaining aqueous portion was diluted to 500.0 ml. Three aliquot portions of 100.0 ml. were analyzed gravimetrically by precipitation with silver nitrate. The chlorine content was found to be 22.5%. A 25.00 ml. sample of the aqueous solution was analyzed volumetrically and the chlorine content by this method was found to be 23.5%. The calculated value for α-chlorostyrene was 25.6%.

Preparation of 2,4-Dichloroacetophenone

1) From 2,4-Dichlorobenzaldehyde and Methyl Magnesium Iodide

This preparation was adapted from the method given by Marshall (12) for the synthesis of acetophenone in small yields.

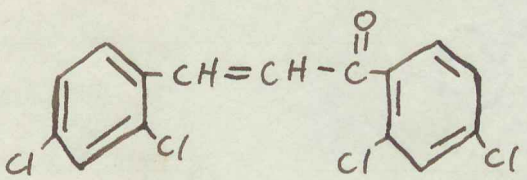
A one l. three neck flask was fitted with a reflux condenser and thermometer. The flask was charged with 12 g. magnesium turnings and 20 ml. of a mixture of 72 g. methyl iodide and 100 ml. anhydrous ether. When the first reaction subsided the remaining methyl iodide-ether solution was slowly added. When the addition was completed the reaction mixture was heated gently until the magnesium dissolved.

The solution was cooled on an ice bath and a solution of 90.4 g. 2,4-dichlorobenzaldehyde in 100 ml. anhydrous

ether and 350 ml. benzene was slowly added, keeping the temperature under 15°. The green reaction mixture was allowed to stand over night. Another solution of 82.4 g. 2,4-dichlorobenzaldehyde in 400 ml. benzene was added keeping the temperature under 5°. The mixture was refluxed for 12 hours at 65°. The brown mixture was then cooled and decomposed with 5 l. of 15% sulfuric acid solution and dissolved in 4.3 l. of benzene. The benzene solution was separated and washed with dilute sodium bisulfite solution, sodium carbonate solution and finally water.

In order to remove any 2,4-dichlorophenylmethylcarbinol that may have formed, a 3 l. portion of the benzene solution was placed in a 3 l. flask with 270 g. anhydrous powdered $CaCl_2$ and stirred for 5 hours. This solution was then decanted from the $CaCl_2$ and distilled to dryness. The solid residue was recrystalized from benzene and washed with several portions of petroleum ether. Light yellow crystals were obtained, weighing 53 g. having a melting point of 140°. Although no further investigation was made, it was concluded that compound was a phenyl styryl ketone, a condensation product of the acetophenone and the unreacted benzaldehyde.

Figure II.



According to Marshall (12) it should be one of the products of this reaction.

The remaining 2.3 l. portion of the benzene solution was distilled to dryness and washed with a small volume of benzene. In order to remove any unreacted benzaldehyde the solid was refluxed for four hours with saturated aqueous sodium bisulfite solution, during which time fine yellow crystals formed. The crystals were collected in a filter and washed with 2 l. of water to remove any bisulfite addition compound of benzaldehyde. The remaining crystals had a melting point of 140°-147° and lacked the distinctive odor of 2,4-dichlorobenzaldehyde. These crystals were distilled from a 125 ml. distilling flask at 5 mm. and the fraction boiling between 120°-128° was collected. The solidified filtrate was recrystalized from benzene, forming white crystals melting between 55°-56°. It was concluded that this compound was 2,4-dichlorophenylmethylcarbinol. Look and Beck (11) give m.p. 74.5° (p-nitrobenzoate m.p. 113°) the boiling point determined by the percolator cup method was found to be 245°.

The α-naphthylurethan was prepared as given in Shriner and Fuson (16). One gram of the carbinol was placed in a test tube with 0.5 ml. α-naphthylisocyanate and warmed on a steam bath for 3 minutes. The urethan was crystalized by cooling the test tube in a beaker of ice. The crystals were collected and recrystalized from hot petroleum ether. White crystals were obtained, m.p. 149°-151°.

In this synthesis no 2,4-dichloroacetophenone was isolated.

2) From 2,4-Dichlorobenzoyl Chloride and Me.Mg.I.

This attempted preparation was adapted from the method developed by Gilman and Mayhue (6).

A 500 ml. 3-necked flask was fitted with a motor stirrer, dropping funnel and a reflux condenser. The flask was charged with 104.8 g. (.5 mole) of 2,4-dichlorobenzoyl-chloride in 75 ml. ether. One half mole of methylmagnesium iodide, as prepared in the previous synthesis using the same quantity of reactants, was placed in the dropping funnel and added slowly with stirring, but without cooling. The addition took one hour, which was fast enough to keep the ether boiling without external heat. After the addition was completed the reaction mixture was refluxed for 4 hours at 37°.

The reaction mixture was then poured into a beaker containing ice and dilute hydrochloric acid. The ether layer was separated and washed with sodium bicarbonate solution to remove any benzoic acid formed from the benzoyl chloride, sodium bisulfite solution to remove iodine, and finally water. The etherial solution was dried over anhydrous sodium sulfate and the ether distilled off. The residue of yellow crystals was recrystalized twice from petroleum ether. The final produce was a white powder melting between 119.5-120.5. As 2,4-dichloroacetophenone melts at about 50°, it was reasoned that the produce obtained was the tertiary alcohol, 2,4-dichlorophenyldimethylcarbinol.

The sodium bicarbonate washings were acidified with hydrochloric acid and a cloudy white precipitate of 2,4-dichlorobenzoic acid separated out. Upon

recrystallization from petroleum ether the benzoic acid melted between 155.5°-157.5°.

This synthesis afforded none of the desired acetophenone; the products were instead a benzoic acid and a tertiary alcohol.

3) From 2,4-Dichlorobenzoyl Chloride and Dimethyl Cadmium

As shown by the last synthesis, the reaction between the methyl magnesium iodide and the benzoylchloride did not produce the substituted acetophenone. Gilman and Nelson (6) have shown that mixed alkyl aryl ketones can be prepared by reacting the benzoyl chloride with dimethyl cadmium. The latter was prepared by the addition of anhydrous cadmium chloride to methyl magnesium bromide.

A one l. flask was set up with a mechanical stirrer with a mercury seal, thermometer, reflux-condenser, dropping funnel, and a gas delivery tube leading to the bottom of the flask. Methyl bromide, a gas at room temperature, was obtained in a steel cylinder. In order to liquefy the gas for weighing, it was passed through a three foot calcium chloride drying column and through a glass tube to the bottom of a one by eight inch stoppered test tube, which was immersed in an ice salt bath. Another glass tube leading from the top of the test tube ran just below the surface of a sulfuric acid trap to exclude the back flow of moisture.

The reaction flask was charged with 8.5 g. (.35 moles) of dried magnesium turnings and 40 ml. absolute ether. Methyl bromide was condensed in the ice salt bath until 24 g. (.36 moles) were collected. The entrance tube to the

condensation test tube was closed and the exhaust tube was attached to the gas delivery tube of the reaction flask. The salt ice bath was removed from the condensation test tube and the methyl bromide was allowed to evaporate at room temperature into the reaction flask. When a vigorous ebullition began an additional 250 ml. absolute ether was added and the mechanical stirrer was turned on.

After the magnesium was dissolved, 35 g. (.19 moles) of anhydrous cadmium chloride, heated strongly to constant weight, was added in small portions to the Grignard reagent with cooling below 10°. A white precipitate of dimethyl cadmium formed. The cooling was removed and stirring was continued for one half hour.

The reaction mixture was cooled over an ice bath and 10.4 g. (.05 moles) 2,4-dichlorobenzoyl chloride in 40 ml. ether was slowly added. Another portion of 41.8 g. (.20 moles) of the benzoyl chloride was added slowly with reflux. The refluxing was continued for one hour.

The reaction mixture was decomposed by pouring into a beaker containing 400 ml. 15% sulfuric acid. The ether layer was separated and washed with water, .5 molar potassium hydroxide, and finally water. The potassium hydroxide washings were continued until no more 2,4-dichlorobenzoic acid precipitated when the washings were discharged into sulfuric acid solution. The ethereal solution was dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residue was a viscose, yellow liquid having a strong odor of benzoyl chloride.

The crude product was boiled with 15% aqueous potassium hydroxide to remove the unreacted benzoyl chloride. The aqueous portion was decanted and discharged into acid which gave a voluminous white precipitate of the benzoic acid. The residue was an orange, viscous liquid. When refluxed with petroleum ether, white particles separated which turned out to be 2,4-dichlorobenzoic acid. The petroleum ether solution, when evaporated on a water bath, yielded a red liquid with a strong odor of benzoyl chloride.

It was concluded that no reaction took place between dimethyl cadmium and 2,4-dichlorobenzoyl chloride. Most of the benzoyl chloride was hydrolized to the benzoic acid.

4) Preparation of 2,4-Dichloroacetophenone from m-Dichlorobenzene and Acetyl Chloride

The Friedel and Crafts ketone synthesis using a hydrocarbon, acetyl chloride, and aluminum chloride is very well known. Roberts and Turner (15) prepared several isomeric dichloroacetophenones and Leonard and Boyd (10) prepared the 2,4 compound by this method.

Preparation of m-Dichlorobenzene

Because of the large expense involved in the purchase of this compound, it was necessary to synthesize it. A good yield was obtained from the diazotation of m-chloroaniline followed by the Sandmeyer Reaction. This method was adapted from Marvel and McElvain (14).

Preparation of Cuprous Chloride

Copper Sulfate (Pentahydrate) 500 g. was dissolved in

a 5 l. round bottom flask with 1600 ml. water. Then 140 g. sodium chloride was dissolved in the hot solution. A solution of sodium sulfite was prepared from 98 g. sodium bisulfite, 75 g. of sodium hydroxide, and 800 ml. of water and was added fairly slowly to the hot copper sulfate. When the solution became decolorized it was cooled and the cuprous chloride was allowed to settle out. The supernatant liquid was decanted, the crude material washed with water by decantation, and finally dissolved in 600 ml. concentrated hydrochloric acid.

Diazotization

The hydrochloride of m-chloroaniline was prepared by the addition, with mechanical stirring, of 204 g. (1.6 moles) of the amine to 400 ml. concentrated HCl and 200 ml. water in a 2 liter round bottom flask. The hydrochloride crystals separated upon cooling in a salt ice bath and the addition of ice. A solution of 112 g. sodium nitrite in 320 ml. water was added with stirring over a period of 10 minutes, keeping the temperature below 5°. The resulting reaction product, m-chlorobenzenediazonium chloride, was dark brown and gave a purple color to starch-KI paper, indicating that the amine hydrochloride had been consumed and nitrous acid was in slight excess.

Sandmeyer Reaction

The solution of cuprous chloride was cooled and into this was poured, with stirring, the diazonium chloride. The resulting mixture was allowed to come to room temperature and after 10 minutes was heated on a steam bath with stirring.

With heating, nitrogen was evolved and the heavy brown addition product decomposed to form an oily layer of m-dichlorobenzene.

The oily layer was decanted into a 2 l. round bottom flask and steam distilled. The ratio of water to m-dichlorobenzene in the distillate was about 5 to 1. The organic portion was separated and washed twice with an equal volume of concentrated sulfuric acid to remove m-chlorophenol and the azo compound. The product was washed with water, dried over anhydrous $CaCl_2$, and distilled, using an air condenser. The fraction boiling between 172° and 175° was collected. The purified product weighed 182 g. giving a yield of 77.6%.

Preparation of 2,4-Dichloroacetophenone

A 500 ml. 3 neck flask was equipped with a dropping funnel, thermometer, motor stirrer, and a reflux condenser fitted with an HCl trap (a gallon jug with a glass tube running to the surface of the water). In the flask were placed 100 g. (.68 moles) m-dichlorobenzene and 100 g. (.74 moles) anhydrous aluminum chloride. Over a period of one hour 50 g. acetyl chloride were added with stirring. A slight temperature rise was noted. The cloudy, yellow mixture was heated to 100° on a water bath and an additional 25 g. portion of acetyl chloride (a total of 75 g., .96 moles) was added over a period of one hour. The reaction mixture, which became clear and red on heating, was stirred for 2½ hours at 100° and then allowed to cool.

The aluminum chloride complex was decomposed by pouring into a 2 l. beaker containing ice and hydrochloric acid. The oil which separated was extracted with ether and the extractions washed with water, sodium hydroxide solution, and again with water. The etherial solution was dried over anhydrous magnesium sulfate and the solvent removed by distillation. The crude product was fractionated through a 6 inch column packed with glass helices and the fraction boiling between 118° and 121° at 7 m.m. was collected. The purified 2,4-dichloroacetophenone weighed 78 g. giving a yield of 62% of the theoretical.

Preparation of 2,4-Dichloro-α-chlorostyrene

A 500 ml. 3 neck flask was fitted with a motor stirrer equipped with a mercury seal, thermometer, and a reflux condenser with an HCl trap. A solution of 32 g. (.165 moles) 2,4-dichloroacetophenone in 75 ml. petroleum ether and 34.5 (.165 moles) PCl_5 were placed in the flask and refluxed with stirring for 2½ hours. During this time the temperature rose from 48° to 62° and the initially cloudy solution became clear as the PCl_5 completely dissolved.

The solvent was distilled off and the residue was distilled at reduced pressure using a water vacuum pump. The portion boiling between 113° and 146° at 16 mm. was collected and fractionated through a 6 inch column packed with glass helices. The four fractions collected (see chart below), distilled over colorless, but soon turned a yellow green.

The chlorine content of each fraction was determined by dissolving the sample in alcohol and boiling with saturated alcoholic silver nitrate. The silver chloride precipitate was collected and weighed in frittered glass crucibles. In this determination the silver nitrate attacked only the chlorine atoms on the α position of the side chain and not the chlorine atoms on the benzene nucleus. The results are as follows:

Fraction	Boiling Point	Pressure	Weight	%Chlorine
I	110°-115°	8 mm.	4 g.	3.50
II	105°-112°	5 mm.	7 g.	4.84
III	115°-125°	6 mm.	15 g.	10.3
IV	125°-130°	6 mm.	5 g.	5.27

The chlorine content of the pure compound was calculated to be 17.5%.

Fraction number III was considered to be richest in 2,4-dichloro-α-chlorostyrene. The boiling point at 760 mm. was 256° and turned dark red upon standing in a stoppered test tube for several days.

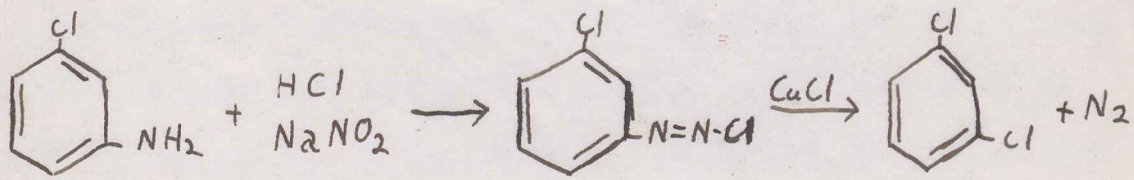
In an attempt to increase the yield of 2,4-dichloro-α-chlorostyrene a second trial was made. In this run the same quantity of reactants were used, but the reaction time was increased from 3.5 to 4.5 hours. When fractionated through a 6 inch column, practically all of the material distilled over at 96°-97° at 5 mm., which indicated that a pure compound was present. A chlorine analysis indicated

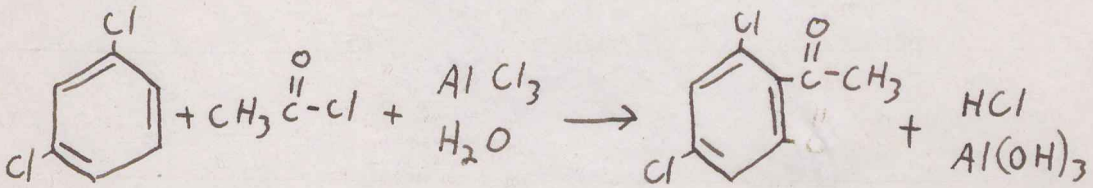
only 0.31%, therefore this compound was not the -chlorostyrene.

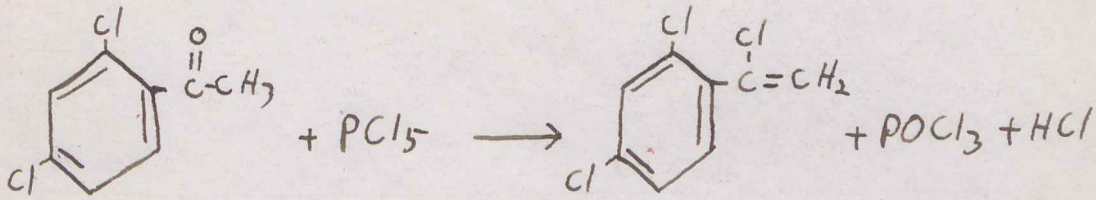
The probably explanation of this anomalous result is that the prolonged reaction time allowed the 2,4-dichloro--chlorostyrene that formed to decompose into 1,2,4 trichlorobenzene, boiling point 215°. The boiling point of the compound obtained was 220°-225°.

The reactions leading up to the preparation of 2,4-dichloro- -chlorostyrene are as follows:

Figure III







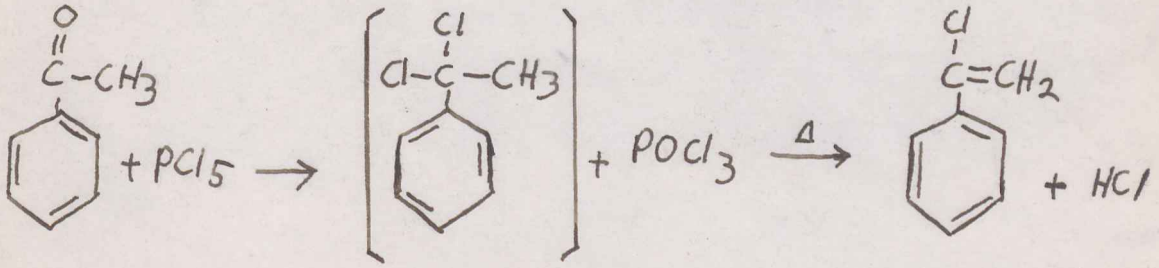
Attempted Polymerization

It was attempted to copolymerize 2,4-dichloro-α-chlorostyrene with several monomers and two different types of catalysts. One-half milliliter portions of methyl methacrylate, vinyl isopropyl ether, and vinyl acetate were placed in 3 inch test tubes with 0.5 ml. of the α-chlorostyrene and .02 ml. of 45% boron trifluoride in ether as the catalyst. The same solutions were also prepared using the peroxide catalyst, Lupersol FDM and Accelerator B. The test tubes were heated over a water bath to 70° for four hours. At the end of this time it was noted that the samples containing boron trifluoride had turned black and those containing the Lupersol had become yellow. No solid material was observed in any of the samples, so it was concluded that no copolymerization had taken place.

DISCUSSION

The synthesis of α-chlorostyrene and nuclear substituted α-chlorostyrenes as developed by Dufraisse and Viel (3) involves the equimolecular reaction between acetophenone and phosphorous pentachloride. In this unique reaction the phosphorous pentachloride removes an atom of oxygen and hydrogen to form the double bond and also serves as a chlorination agent for the α carbon atom. The probable mechanism for this reaction is as follows:

Figure IV



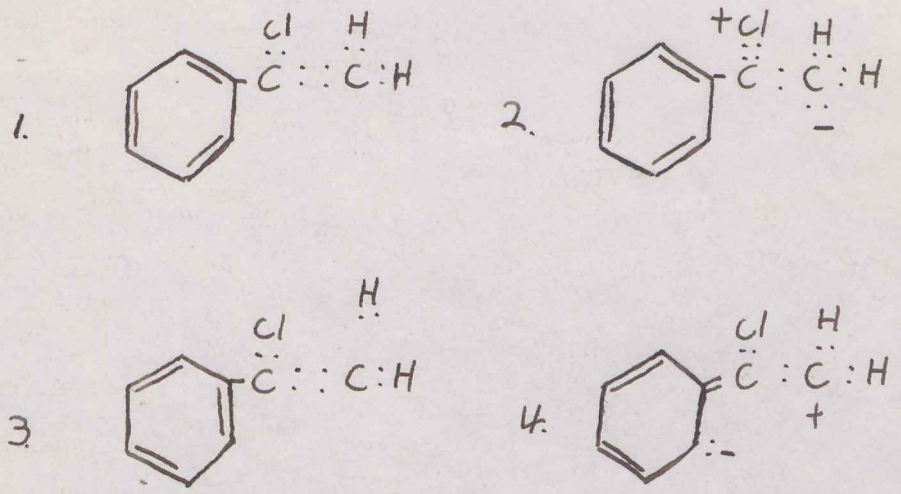
A dichloro intermediate is formed which is probably thermally unstable and splits off hydrogen chloride to give the more stable α-chlorostyrene. This compound is also somewhat unstable, as it slowly decomposes on standing at room temperature and at elevated temperatures this decomposition is greatly accelerated. The products of decomposition according to Dufraisse and Viel are chlorobenzene and formaldehyde. Further evidence for the

instability of substituted and unsubstituted α-chlorostyrene is the extremely low yield of the 2,4-dichloro compound when the reaction time at elevated temperatures was increased.

If the hydrogen chloride concentration of the reaction mixture is not kept at a minimum readdition will take place across the double bond to form the intermediate dichloro addition compound. This was prevented by using petroleum ether as a solvent, in which hydrogen chloride is insoluble.

As might be expected the α -chlorine atom is somewhat reactive toward electrophilic reagents because of its position on a conjugated system. The reactivity is only slightly decreased by resonance stabilization of the molecule. The greatest contribution is from structure 1, with a very slight amount coming from 2, 3, and 4, Figure V.

Figure V



The main interest in α-chlorostyrenes, however, is not the reactivity of the α-chlorine atom, but in polymerization and copolymerization. Attempts by Marvel, Inskeep, et. al. (15) and Coleman employed electrophylic and radical reagents, but did not note any polymerization.

This failure to polymerize may be explained partially by steric blocking. The α-chlorine atom because of its position limits the direction from which the double bond can be attacked and also the size of the attacking molecule. The validity of this explanation may be questioned, as α-methylstyrene, which also has a large group on the α carbon atom, will polymerize under the influence of nucleophillic and radical reagents and is therefore not sterically hindered.

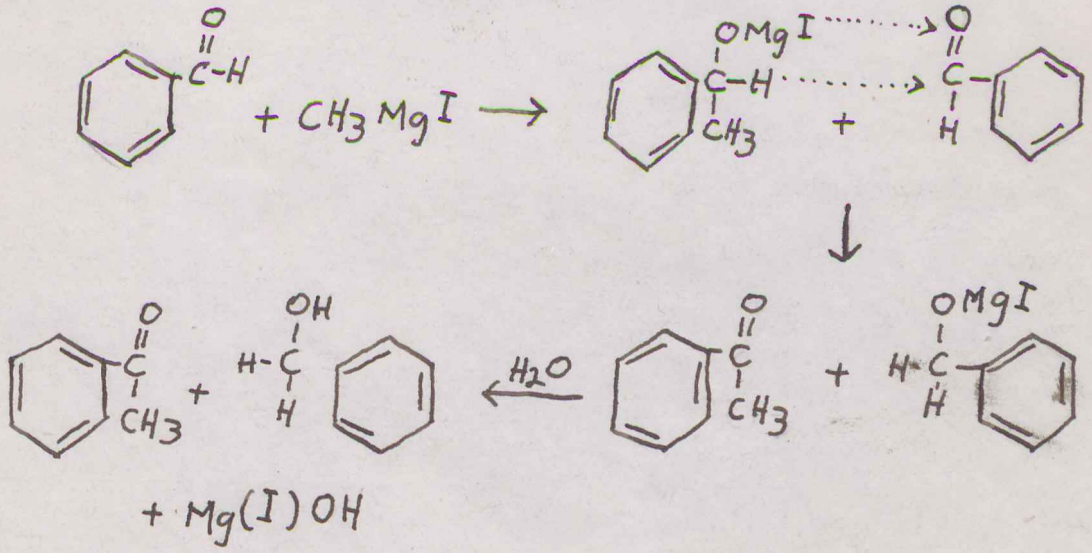
The inductive effect of the substituent on the α carbon atom undoubtedly has effect on the ease of polymerization. Styrene will readily polymerize under the influence of electrophylic reagents (stannic chloride), radical reagents (benzoyl peroxide), and nucleophilic reagents (triphenyl methyl sodium), while α methylstyrene will polymerize only under the influence of a nucleophilic catalysts, and α-chlorostyrene will not polymerize at all. The molecule with the greatest reactivity toward polymerization has the α substituent of the least electronegativity, while the molecule with the least reactivity has the greatest electronegative α substituent. The effect of the α hydrogen atom on styrene does not alter

the electron configuration of the double bond on the side chain, while the α chlorine atom on the α-chlorostyrene molecule tends to "attract" an electron pair away from the double bond between the α and β carbon atoms through the Inductive Effect.

Structures 2 and 4, Figure V, which contribute slightly to the overall structure, also tend to remove an electron pair from the α , β double bond. An attack by a polymerizing agent would tend to split off the β carbon atom. These structures, then, tend to inhibit polymerization.

The reaction of benzaldehyde and methylmagnesium iodide is the addition of the Grignard reagent across the carbonyl bond giving phenylmethyl carbinol as the product. According to Marshall (12), when an excess of the aldehyde is employed a disproportionation takes place as follows:

Figure VI



The products being acetophenone and benzyl alcohol. As Marshall did not report the percent yield, it is assumed that it was quite small.

In the present investigation this reaction was attempted using 2,4-dichlorobenzaldehyde. As was reported, the only product obtained was the dichlorophenylmethylcarbinol and not the acetophenone. The explanation of this is largely a steric effect, as there undoubtedly is considerable steric hinderance between the number 2 chlorine atom and the carbonyl group.

The substitution of halogen atoms in the ortho and para positions to an acyl chloride group on a benzene ring tends to reduce the reactivity of the "acid" chlorine atom to a marked extent. This can be illustrated by the hydrolysis of benzoyl chlorides. Benzoyl chloride itself hydrolyses quite readily in hot water, while the 2,4-dichloro compound is hydrolyzed only upon boiling with potassium hydroxide solution. As cited by Hickinbottom (8), 2,4,6-tribromo benzoyl chloride is only converted to the extent of 28% after boiling with water for 30 minutes.

This reduction of reactivity may be simply explained by the opposition of Inductive Effects between the chlorine atoms on the benzene nucleus and the "acid" chlorine atom. Both are attempting to attract electrons from other parts of the molecule. The net result is that the "acid" chlorine atom is bound tighter to the α carbon atom. This theory is substantiated by the reaction of 2,4-dichlorobenzoyl chloride

and methylmagnesium iodide. Addition across the carbonyl bond takes place before the replacement of the "acid" chlorine atom by the methyl group; the final product being the tertiary alcohol, 2,4-dichlorophenyldimethylcarbinol and not the desired acetophenone.

According to Hickinbottom (9), cadmium dialkyls react preferentially with the "acid" chlorine atom instead of the carbonyl group of an acid chloride. The reaction between dimethyl cadmium and 2,4-dichlorobenzoyl chloride, conducted in the present investigation, gave only the benzoic acid and the unreacted acid chloride. As the dimethyl cadmium was not active enough to add across the carbonyl group the only other alternative was to react with the "acid" chlorine atom, but the "acid" chlorine atom was so stabilized by the Inductive Effect that no reaction takes place.

The structure of the 2,4-dichlorobenzoyl chloride atom is such that there is steric hinderance between the "acid" chlorine and the number 2 nuclear chlorine atom. This also helps to explain the lack of reactivity of the "acid" chlorine atom.

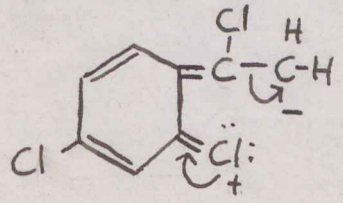
The reactions leading up to the preparation of 2,4-dichloroacetophenone from m-chloroaniline do not require any discussion at this point, while the conversion to the 2,4-dichloro-α-chlorostyrene is analogous to the synthesis of the unsubstituted α-chlorostyrene, which has been treated in some detail. The only pertinent difference is the relatively greater instability of the disubstituted

compound at elevated temperatures. This is indicated by the low yield when the reaction time at higher temperatures is increased.

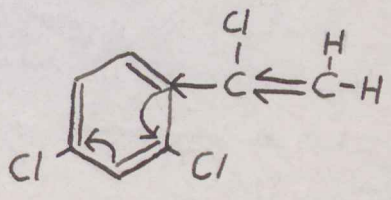
Coleman (2) and Marvel, Inskeep, et. al. (13) have illustrated the inability of α-chlorostyrene to polymerize or copolymerize. At the outset of the present investigation it was hoped that the substitution of chlorine on the benzene ring of α-chlorostyrene would improve the polymerization qualities. The contributions from structures 2 and 4, Figure V, tend to equalize each other, leaving no active center for the polymerizing agent to attack. It was thought that the nuclear chlorine atoms would unbalance the system through the Inductive Effect allowing an attack on the side chain. The tests conducted on 2,4-dichloro-α-chlorostyrene, although by no means conclusive, indicate that no copolymerization takes place using a peroxide (radical catalyst) and boron trifluoride (electrophilic catalyst).

In addition to the resonance structures possessed by the unsubstituted compound, which hinder polymerization, the 2,4-dichloro compound also has a contribution from the following structure 1, Figure VII, which removes an electron pair from the α, β double bond.

Figure VII



1.



2.

The Inductive Effect of the nuclear chlorine atoms also contribute to the removal of an α,β electron pair, structure 2, Figure VII.

Polymerization is undoubtedly also retarded by steric hinderance. When 2,4-dichloro-α-chlorostyrene was constructed out of Fischer Hirschfelder Atomic Models, there was a physical blocking between the number 2 chlorine atom on the nucleus and the α chlorine and the β carbon atom. The rotation of the side chain about the benzene ring was limited to about 180°. The plane of the α,β double bond was perpendicular to the plane of the benzene ring, so that one side of this bond was completely protected from an attacking molecule by the number 2 nuclear chlorine atom.

SUMMARY

1) Several methods of preparation of 2,4-dichloroacetophenone were examined. A high yield of this compound was obtained by the Friedel and Crafts reaction of m-dichlorobenzene and acetyl chloride.

2) The preparation of α-chlorostyrene and 2,4-dichloro-α-chlorostyrene have been carried out by the equimolecular reaction of phosphorous pentachloride and the appropriate acetophenone. The physical constants of α-chlorostyrene were determined.

3) It was shown that 2,4-dichloro-α-chlorostyrene does not copolymerize with the several monomers used and peroxide and boron trifluoride catalysts.

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